AN INVESTIGATION OF THE THERMAL
PROPERTIES OF AMMONIA

BY

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THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPER-

VISION BY ___Frank Gustave Wahlen___

ENTITLED _An Investigation of the Thermal Properties of_

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DEGREE OF__Master of Science in Mechanical Engineering__

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*Required for doctor's degree but not for master's.

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AN INVESTIGATION OF THE THERMAL PROPERTIES OF AMMONIA

I. Earlier Investigations

Consistent formulations of the thermal properties of ammonia have been made by Goodenough and Mosher, (Bulletin 66, University of Illinois Experiment Station) and by Keyes and Brownlee, (The Thermodynamic Properties of Ammonia, Wiley 1916). Both are based on the then existing data and both correlate the various properties of ammonia through thermodynamic laws. In Goodenough and Mosher's treatment, the pressure and temperature are taken as the independent variables and all the properties are expressed as functions of the pressure and temperature. In Keyes and Brownlee's treatise, the volume instead of the pressure and temperature is taken as the independent variable. This choice has a theoretical advantage of giving a characteristic equation which is of third degree in the volume and may therefore, like van der Waals' equation, represent the liquid volume as well as the vapor volume; it also has the practical disadvantage of greatly complicating the mathematical operations.

Both formulations are consistent, but as to their accuracy, the then existing data gave no basis of comparison.

II. Bureau of Standards' Data

In Bulletins 313 and 315, the U.S. Bureau of Standards have published reliable data on the following;

Specific heat of liquid ammonia.

Specific volumes of liquid ammonia.

Specific volumes of ammonia vapor at saturation
temperatures.

Latent heat of vaporization of ammonia.

Bureau of Standards' values for latent heat of vaporization compared with those of Goodenough and Mosher and with those of Keyes and Brownlee,

t	-40	-22	-4	14	32
B. of S.	597.0	584.7	571.7	557.9	543.3
G. & M.	601.9	588.8	575.3	561.2	546.5
K. & B.	615.9	600.6	584.7	568.2	550.9

t	50	68	86	104	122
B. of S.	527.7	510.9	493.0	473.6	451.5
G. & M.	531.0	514.7	497.5	479.2	459.7
K. & B.	532.8	513.8	494.0	472.9	450.3

Bureau of Standards values for specific volumes of ammonia vapor at saturation temperatures compared with those of Goodenough and Mosher and with those of Keyes and Brownlee,

t	-58	-40	-22	-4	14	32
B. of S.	40.845	24.252	15.073	9.808	6.632	4.624
G. & M.		25.45	15.68	10.08	6.72	4.631
K. & B.		25.36	15.62	10.06	6.73	4.650

t	50	68	86	104	122
B. of S.	3.284	2.371	1.764	1.326	1.009
G. & M.	3.278	2.377	1.759	1.325	1.012
K. & B.	3.298	2.393	1.770	1.330	1.011

The most prominent feature of the Bureau of Standards'
results is the decrease in the saturated vapor volumes compared
with the older values due to Dieterici.   The values for the
latent heat run a little lower than the older ones.

Having obtained from the Bureau of Standards, trustworthy
data on latent heat and specific volumes, heretofore lacking, it
is the object of this investigation to revise the Goodenough and
Mosher formulation, using the same general method, and get if
possible a new consistent system of property equations that shall
include the values of the Bureau of Standards' data.

III. Thermodynamic Relations.

Notation;

    J = Joule's equivalent.

    A = Reciprocal of the same.

    t = Temperature on the F. scale.

    T = Absolute temperature.

    p = Pressure in pounds per square foot.

    v = Specific volume in cubic feet per pound.

    i = Heat content at constant pressure.

r = Latent heat of vaporization.

c = Specific heat.

c_p= Specific heat at constant pressure.

(') indicates properties of liquid.

(") indicates properties of saturated vapor.

From the laws of thermodynamics are obtained two all-important relations that are the basis of any formulation of the properties of a vapor.   They are;

(a) The Clapeyron relation,

$$r = AT(v" - v')\frac{dp}{dT} , \qquad (A)$$

in which $\frac{dp}{dT}$ is obtained from the pressure-temperature relation of the saturated vapor.

(b) The Clausius relation,

$$\left(\frac{\partial c_p}{\partial p}\right)_T = -AT \left(\frac{\partial^2 v}{\partial T^2}\right)_P \qquad (B)$$

Let the characteristic equation be given in the form

$$v = f(p,T) \qquad (1)$$

then by two differentiations of (1) holding p constant, the second member of (B) is obtained and from this an expression for c_p may

be deduced. For example, the characteristic equation has been given the form,

$$v = \frac{BT}{p} - \varphi(T) - f(p) \qquad (2)$$

$\varphi(T)$ and $f(p)$ being arbitrary functions that are to be determined from existing data. Then,

$$\frac{\partial v}{\partial T} = \frac{B}{p} - \varphi'(T) \qquad (3)$$

$$\frac{\partial^2 v}{\partial T^2} = -\varphi''(T)$$

$$-AT \frac{\partial^2 v}{\partial T^2} = AT \varphi''(T)$$

$$\left(\frac{\partial c_p}{\partial p}\right)_T = AT \varphi''(T)$$

whence, $\qquad c_p = F(T) + ApT \varphi''(T) \qquad (4)$

where $F(T)$ is an arbitrary function.

A third fundamental equation is the following;

$$di = c_p \, dT - A\left[T \left(\frac{\partial v}{\partial T}\right)_p - v\right] dp \qquad (C)$$

From (2) and (3), the expression in the bracket is,

$$\varphi(T) - T\varphi'(T) + f(p)$$

Introducing this and the expression for c_p given by (4) in (C),

$$di = F(T) \, dT + ApT \varphi''(T) \, dT - A\left[\varphi(T) - T\varphi'(T)\right] dp - Af(p) \, dp \qquad (5)$$

This expression is an exact differential and its integral is,

$$i = F, (T) - Ap\left[\varphi(T) - T\varphi'(T)\right] - Af, (p) + i_o. \qquad (6)$$

in which, $F, (T) = \int F(T)dT$

$f, (p) = \int f(p)dp$

and i_o is a constant of integration.

The equations here developed furnish the analytical machinery by which the available data are to be correlated and, if possible, woven into a consistent system of values. The functions and constants of equation (2) must be so chosen that the equation gives the Bureau of Standards' experimental values of the saturation volumes v'', and also if possible the Perman and Davies' values of the volumes of the superheated vapor. Having this equation settled, the second term of equation (4) is known, and the arbitrary function $F(T)$ is chosen so that equation (4) satisfies as well as may be the scattered and discordant values of the specific heat of superheated ammonia. Finally, the terms in (6) are now known and the values of i_o thus determined are to be compared with the experimental values from the Bureau of Standards.

The following alternative procedure may be followed. Having equation (2) established, the terms involving p in equation (6) may be calculated; then by comparison with the Bureau of Standards' values of i, values of

$$F, (T) + i_o$$

are found. Differentiation of this function gives $F(T)$ one of the

terms in equation (4), and the other term may be calculated.
Then values of c_p thus obtained may be compared with experimental
values.

One important fact following from relation (B) should be
noted. The second derivative $\frac{\partial^2 v}{\partial T^2}$ gives the curvature of the
curve obtained by plotting v against T with constant pressure. If
the curve is a straight line, as in the case of a perfect gas,
the derivative is zero, consequently $\frac{\partial c_p}{\partial p} = 0$, or the specific
heat is independent of the pressure.   If the v-T curve is convex
upward (i.e. negative curvature), the c_p derivative is positive
and the specific heat increases with the pressure, and conversely
if the v-T curve is convex downward (i.e. positive curvature), the
c_p derivative is negative and the specific heat decreases with the
pressure, the more convex the curve is (i.e. the greater the
absolute value of the curvature) the larger the c_p derivative is in
absolute value, and the more the specific heat changes with the
pressure, hence the larger the spacing between the specific heat
curves of any two fixed pressures. Which direction this spacing
takes place depends on whether the specific heat increases or de-
creases with the pressure, which in turn depends on whether the
curve is concave upwards or downwards.

The Clapeyron relation (A) gives a very valuable check as to
whether the pressure temperature equation is properly chosen as
to be consistent, especially since the Bureau of Standards has
given out reliable values of latent heat and specific volume, the

lack of which up to the present time had prevented the employment of its fullest possibilities. All that is necessary now to test a proposed p-T equation is to take its first derivative and substitute in the Clapeyron relation along with the corresponding values for r and v' and solve for v''; if the range of values for v" agrees with the experimental values for v" of the Bureau of Standards, the equation may be pronounced consistent and satisfactory.

IV. Pressure - Temperature Relation

The new data published by the Bureau of Standards affords a means of checking values of the derivative $\frac{dp}{dt}$ in the Clapeyron-Clausius relation;

$$v'' - v' = \frac{Jr}{T \frac{dp}{dt}}$$

Derivatives from Goodenough and Mosher's and from Keyes and Brownlee's investigations based on previous data are not in accord with the new data of the Bureau of Standards. The problem is then to derive an equation $p = f(T)$ such that computed pressure values satisfy experimental pressure values and that values of $\frac{dp}{dt}$ satisfy the Clapeyron-Clausius relation with the new values for latent heat and for specific volumes of the liquid and of the vapor inserted. Prof. Goodenough has attacked this problem and has ob-

tained the following equation and constants;

$$\log p = A + \frac{B}{\theta} + C\theta + D\theta^2 + E\theta^3 + F\theta^4 \quad \text{where } \theta = \frac{T}{100}$$

A = 66.39024

B = -92.16206   log -B = 1.9645522

C = -20.67988   log -C = 1.3155480

D = 3.582443   log D = 0.5541793

E = -0.3132620   log -E = $\bar{1}$.4959077

F = 0.01105736   log F = $\bar{2}$.0436514

This pressure-temperature curve is shown plotted on Plate 1.

Following is a comparison of values calculated from this formula with values given by Keyes and Brownlee and by Goodenough and Mosher.

t	-58	-40	-22	-4	14	32
p calc.	5.695	10.279	17.370	27.813	42.60	62.87
K.& B.	5.757	10.282	17.326	27.710	42.49	62.86
G.& M.	5.72	10.12	16.96	27.13	41.71	61.91

t	50	68	86	104	122
p calc.	89.91	125.15	170.2	226.73	296.6
K.& B.	90.04	125.4	170.5	226.9	296.3
G.& M.	89.09	124.7	170.2	227.7	298.5

Plate 1. Calculated Pressure-Temperature Curve.

t	-58	-40	-27.967	-22	-4	14
p	5.695	10.279	14.697	17.370	27.813	42.62
t	32	50	68	86	104	122
p	62.87	89.91	125.15	170.2	226.73	296.6
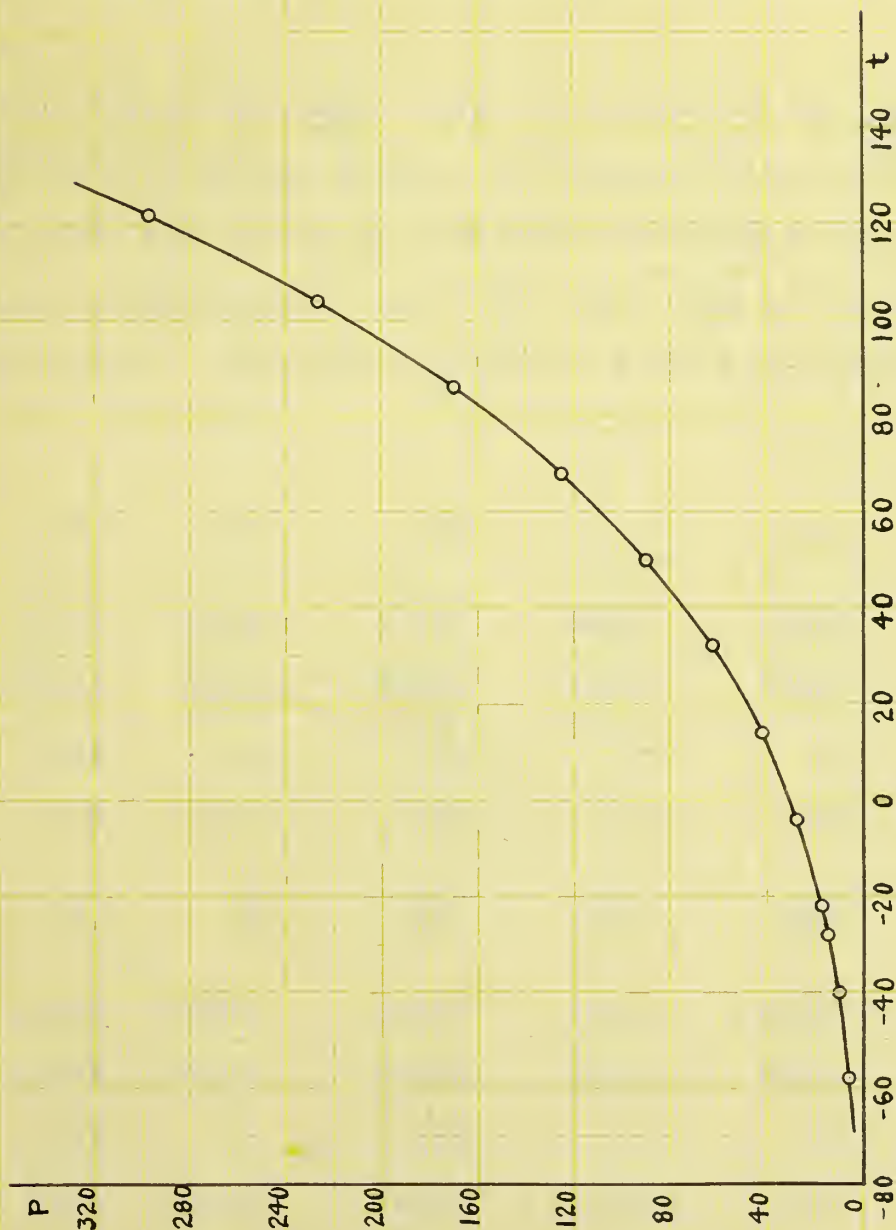
The calculated values agree substantially with those of Keyes and Brownlee and those of Mosher from 122°F down to about -56°F. For still lower temperatures the calculated values appear to be somewhat low.

To check the values for $\frac{dp}{dT}$, take the values of log $\frac{dp}{dT}$ calculated from the preceding formula and compare with the same values deduced from the Bureau of Standards experiments on specific volumes of the liquid and of the vapor and on the latent heat of vaporization.   Only the mantissas of the logarithms are given.

t	-58	-40	-22	-4	14
Cal.	29818	50122	67995	83941	98339
B.of S.	30192	50112	68066	84039	98347
Diff.	-344	10	-71	-98	-8
Diff.%	0.8	0.02	0.16	0.23	0.02

t	32	50	68	86	104
Cal.	11446	23461	34539	44794	54328
B.of S.	11309	23453	34822	44825	54349
Diff.	137	8	-283	-31	-21
Diff.%	0.32	0.02	0.66	0.07	0.05

Again, taking the calculated values of $\frac{dp}{dT}$, the Bureau of Standards formula for latent heat, the B.of S. values of specific

volumes of the liquid and of the vapor, the saturation volumes
may be calculated and compared with the Bureau of Standards'
volumes;

t	-58	-40	-22	-4	14	32
v" cal.	41.169	24.246	15.098	9.830	6.633	4.610
B.of S.	40.845	24.252	15.073	9.808	6.632	4.624
K. & B.		25.36	15.62	10.06	6.73	4.650
Mosher.		25.45	15.68	10.08	6.72	4.631

t	50	68	86	104	122
v" cal.	3.283	2.386	1.766	1.327	1.006
B.of S.	3.284	2.371	1.764	1.326	1.009
K.& B.	3.298	2.393	1.770	1.330	1.011
Mosher	3.278	2.377	1.759	1.325	1.012

A plot showing these values is given on Plate 2, where Perman
and Davies' curve of volumes of superheated ammonia at atmospheric
pressure is also shown.

V. Saturation Volume at Atmospheric Pressure.

The next step is the determination of the temperature corres-
ponding to atmospheric pressure (14.697 lb. per sq. in.) from the
pressure-temperature equation. As this equation gives the tempera-
ture corresponding to any given pressure implicitly, it was

Plate 2. Calculated Volume-Temperature Curve with
Perman and Davies' Superheat Curve at Atmospheric Pressure.

t	-58	-40	-27.967	-22	-4	14
v	41.169	24.246	17.5678	15.098	9.830	6.633

t	32	50	68	86	104	122
v	46.10	3.283	2.386	1.766	1.327	1.006

Perman and Davies'   Points.

t	-4	32	122	212
v	19.154	20.780	24.785	28.775
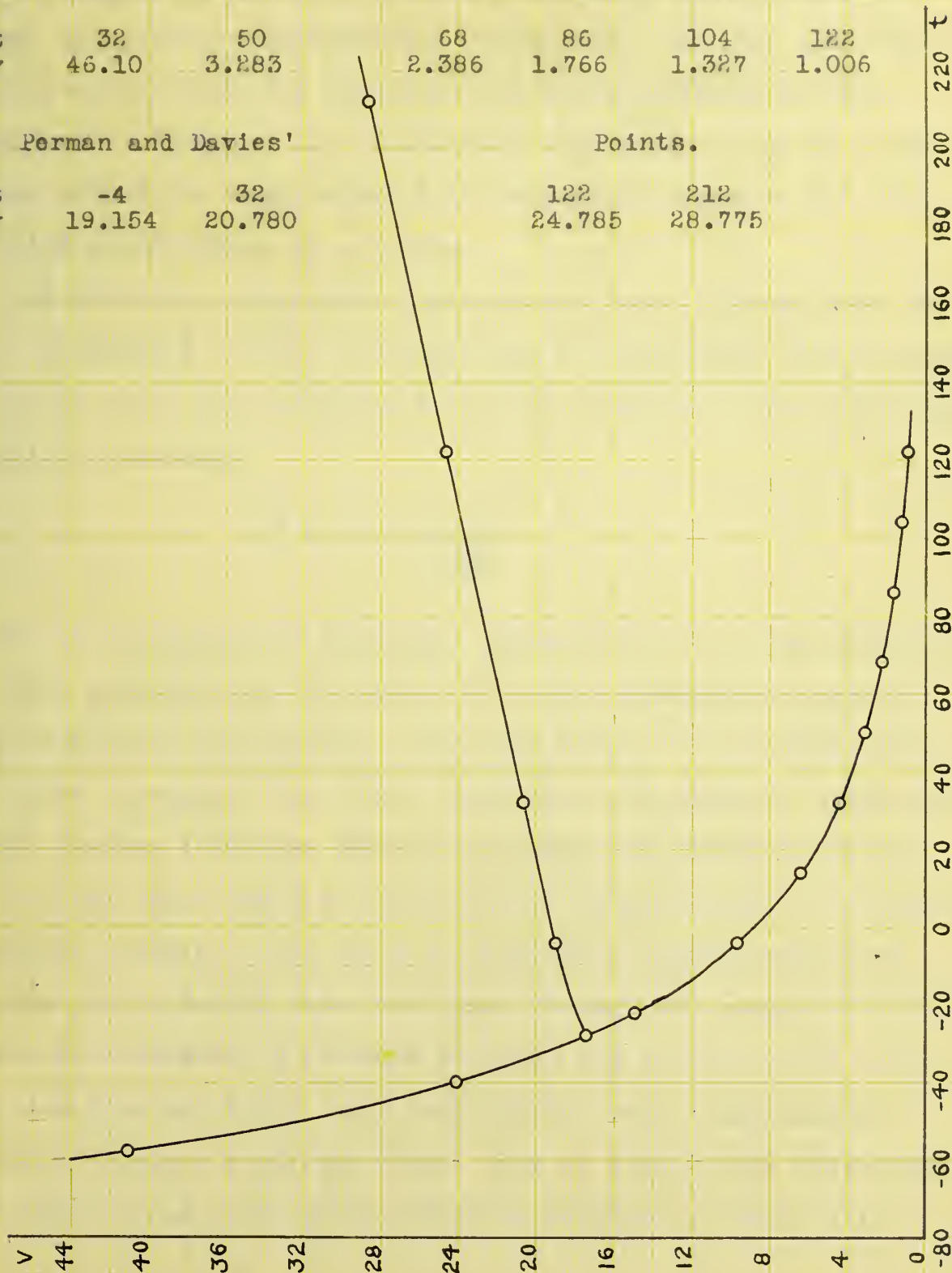
thought best to obtain the temperature value by interpolation; hence the pressure values for t = -25, -26, -27, -28, -29, -30, were obtained from the equation, the sixth differences were examined to see that the values were consistent, then by a well-known method the temperature for atmospheric pressure was interpolated and found to be -27.967.

The pressure-temperature equation was then differentiated and the temperature -27.967 corresponding to atmospheric pressure was inserted; then the resulting value was inserted in the Clapeyron-Clausius relation,

$$v'' - v' = \frac{J\ r}{T\ \frac{dp}{dt}}$$

With the new Bureau of Standards' values for v', r, the solution of this equation gave the value of v'' for atmospheric pressure and saturation temperature. This was found to be 17.5678, which is quite different from 17.97, Goodenough and Mosher's value and still further different from 18.16, Keyes and Brownlee's value.

To check this computed value of v'', the new Bureau of Standards' specific volumes of the vapor at saturation temperatures were plotted and a smooth curve was drawn through the points; then the value for atmospheric pressure (14.697) was read from the curve and found to be 17.57. All computations were independently checked at three different times, once by seven-place logarithms and twice by an eight-place computing machine, so that it is

extremely unlikely that the computed values for the saturation
temperature at atmospheric pressure and the specific volume at
atmospheric pressure and saturation temperature are in error.

VI. The Characteristic Equation.

The next problem was to take this value of v" at atmospheric
pressure and saturation temperature together with Perman and
Davies' superheat values of the specific volumes at atmospheric
pressure and find a suitable equation of the curve passing
through these points.   Let $\psi(T)$ denote the function representing
this curve.   The forms of the function $\psi(T)$ tried were the
following;

$$\frac{m}{T^n} + bT + c = \psi(T)$$

where the different values for n tried were 2,4,5,6, and 10.

$$\frac{m}{(t-110)^4} + bT + c = \psi(T)$$

$$\frac{m_1}{T^r} + \frac{m_2}{T^s} + bT + c = \psi(T)$$

where the different pairs of values for r,s, tried were 2,1;4,2;
4,3; 3.5,3; 5,3; 5,4; 6,4; and 6,5.

Each of these would pass the curve through the points quite
well. It was found, however, that the v-T superheat curve (Plate
4) if made to pass through the saturation point and Perman and
Davies' first point had so great a curvature near the saturation

limit that an attempt to satisfy the Clausius relation

$$\left[\frac{\partial\ c_p}{\partial\ p}\right]_t = -AT \left[\frac{\partial^2 v}{\partial\ T^2}\right]_p$$

gave an increase of c_p with the pressure that seemed altogether improbable.

Each of the equations tried for $\psi(T)$ obviously has its own individual values for m, m_1, m_2, b, c. The way in which the $\psi(T)$ enters into the v equation

$$v = \frac{BT}{p} - \varphi(T) - f(p)$$

is that $\frac{B}{p} = b$, $-f(p) = c$, $\varphi(T) =$ the term with coefficient m or the two terms with coefficients m_1 and m_2.

The specific volume of the vapor at atmospheric pressure and saturation temperature as taken from Goodenough and Mosher's ammonia tables is 17.97. This taken with Perman and Davies' points necessitates an equation which when put through the Clausius specific heat relation gives a comparatively wide spacing for the specific heat curves at constant pressure, although no where near as wide as the spacing obtained by the preceding point (17.5678) based on the Bureau of Standards' data.

The specific volume of the vapor at atmospheric pressure and saturation temperature as interpolated from Keyes and Brown-lee's tables is 18.16. This value plotted with the Perman and Davies' points gives a curve which is concave upward, hence its

second derivative is positive and thus when put in the Clausius
specific heat relation gives a negative spacing of the c_p curves.
On the other hand, in Keyes and Brownlee's book is shown a
diagram of specific heat curves at constant pressure in which the
spacing is positive.

It is possible that Keyes and Brownlee may have departed
from Perman and Davies' points sufficiently to secure a curve
convex upward.   A chart showing the deviation of the Keyes and
Brownlee's values from the Perman and Davies' values is given on
page 20 of Keyes and Brownlees' book.   Taking account of these
deviations helps matters a little but does not seem to clear up
the apparent discrepancy entirely.   The Keyes and Brownlee
approximation to the Perman and Davies' points are 19.164, 20.822,
24.735, 28.631.   These are shown plotted with the atmospheric
saturation point on Plate 3.

Plate 4 shows the Perman and Davies' points plotted with
the atmospheric points of Goodenough and Mosher, Keyes and Brown-
lee, and the new Bureau of Standards' point.

Here exists an inconsistency that cannot be reconciled. If
the Bureau of Standards' saturation value $v = 17.5678$ cu. ft. is
accepted as correct and Perman and Davies first points, namely
$v = 19.154$ and $v = 20.780$ are also accepted, then the v-T curve
(plate 4) shows a curvature quite inconsistent with the possible
variation of the specific heat.   It is probable that greater

Plate 3. Keyes and Brownlee's Specific Volume Curve
at Atmospheric Pressure.

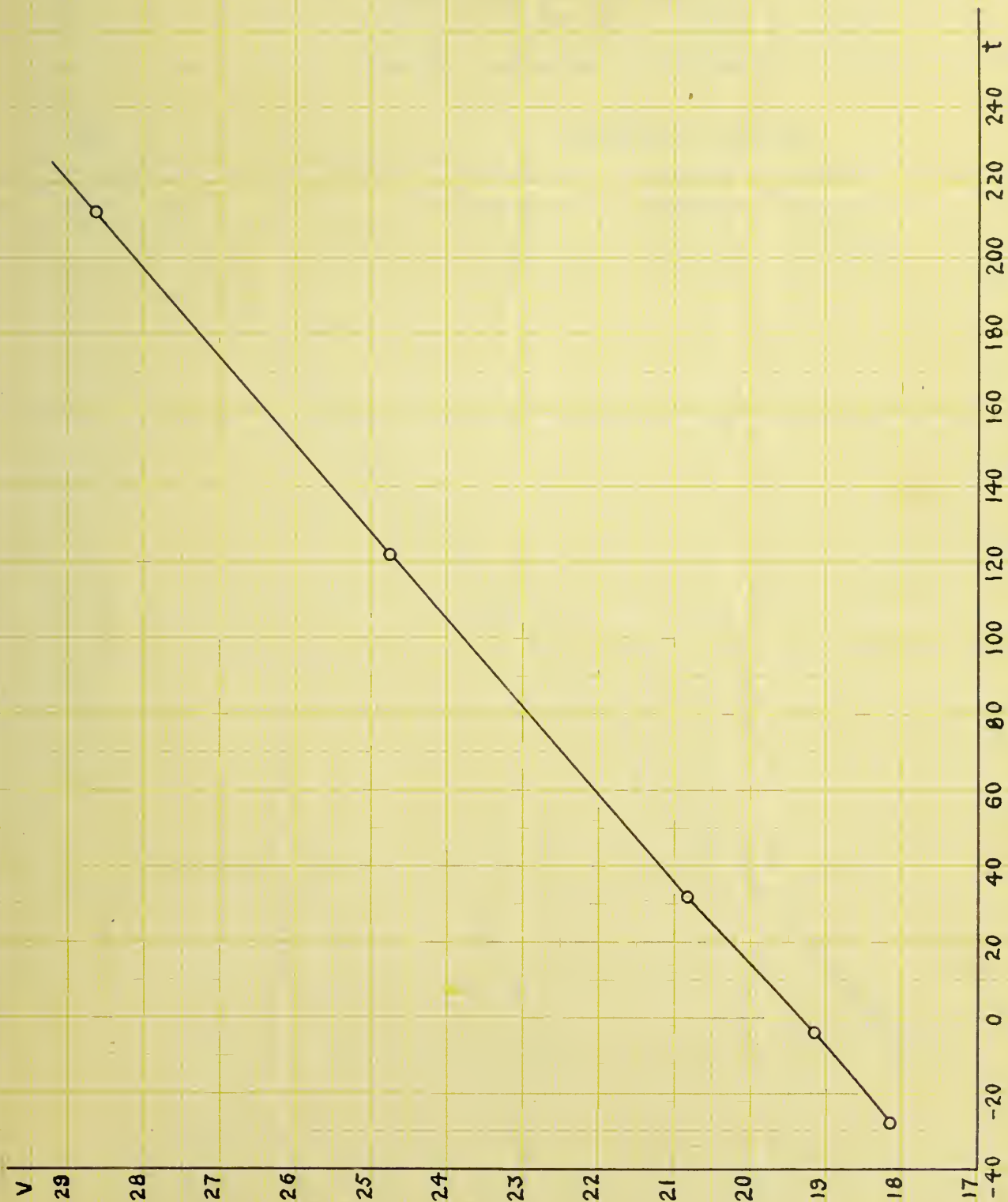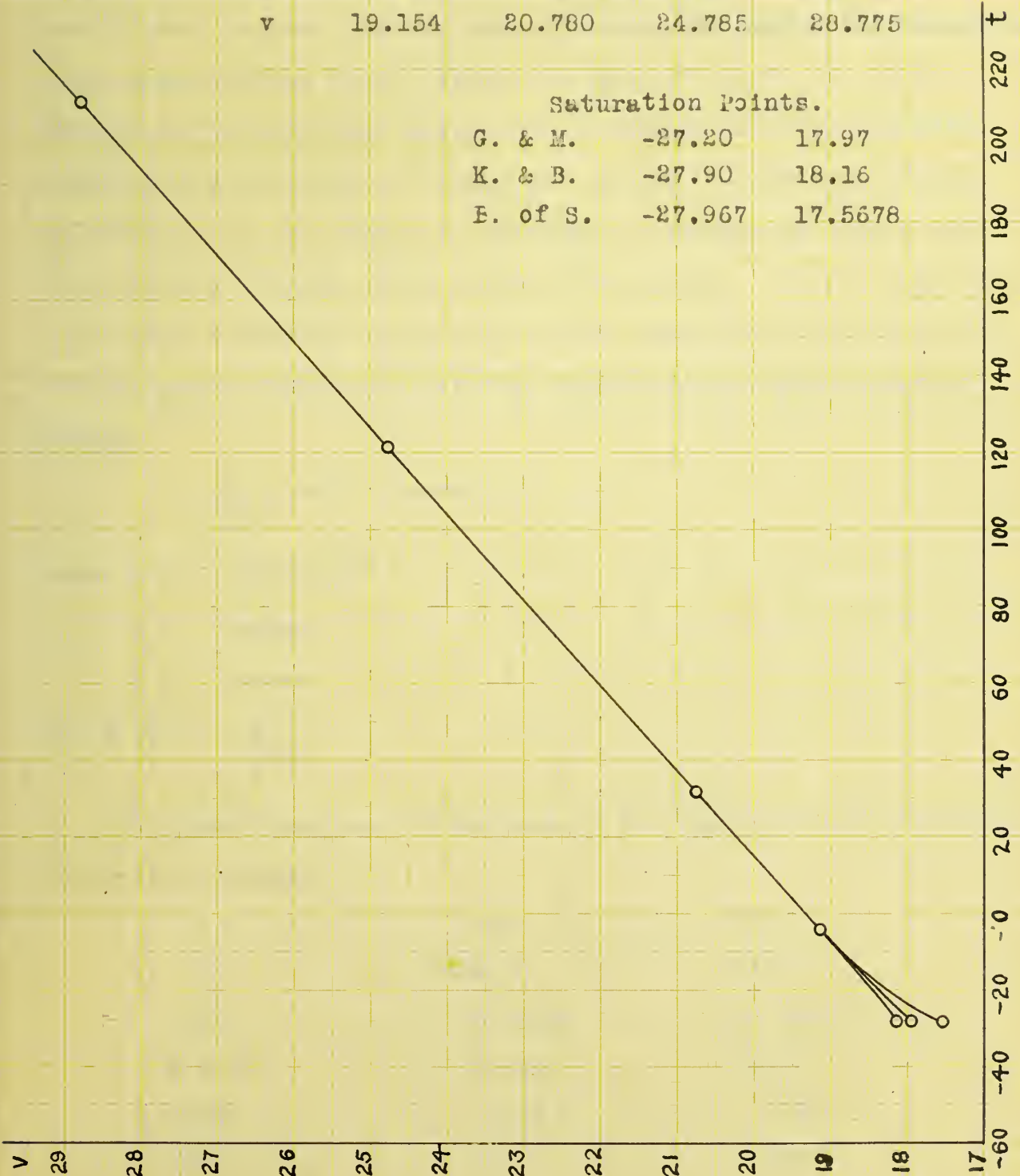| t	-27.90	-4	32	122	212
v	18.16	19.164	20.822	24.735	28.631

Plate 4. Perman and Davies' Specific Volume Superheat
Curve at Atmospheric Pressure with Various Saturation
Temperature Points.

Perman and Davies' Points.

t	-4	32	122	212
v	19.154	20.780	24.785	28.775

Saturation Points.

G. & M.	-27.20	17.97
K. & B.	-27.90	18.16
B. of S.	-27.967	17.5678

weight should be attached to the Bureau of Standards' value than
to the Perman and Davies' points.   It is, therefore, considered
justifiable to pass the v-T curve through the Bureau of Standards'
point and entirely below Perman and Davies' first two points.
Therefore, in the final attempt to establish the characteristic
equation the last two of Perman and Davies' points were chosen
and these with the Bureau of Standards' atmospheric point made
three points through which curves were passed.   In the equations
  (T) that represent these curves, the important part is $\psi(T)$.
The following expression for the function $\psi(T)$ was ultimately
chosen;

$$\frac{m}{T^6} + bT + c = \psi(T)$$

where m = $-5.4729 \cdot 10^{15}$

    b =   .043425

    c = -.32947

and $\varphi(T) = \frac{m}{T^6}$

    The following is a comparison of the computed and the Perman
and Davies' values;

t	-4	32
T	455.6	491.6
(T)	18.8429	20.6302
P.& D.	19.154	20.78
Diff.	.311	.15
%Diff.	1.62	.57

The curve passes through the other points exactly. These values are the specific volumes for atmospheric pressure. The general equation for any pressure is;

$$v = \frac{BT}{p} - \varphi(T) - f(p)$$

where $B = b(14.697) = .638214$

$m = 5.4729 \cdot 10^{15}$

$f(p) = c = -.32947$ for $p = 14.697$

$\varphi(T) = \frac{m}{T^6}$

The $f(p)$ is obtained by subtracting the $\frac{BT}{p} - \frac{m}{T^6}$ values for each of the twelve values of the temperature and its corresponding saturation pressure value from the calculated volume obtained from the pressure-temperature equation by means of the Clapeyron relation. The differences are paired up with their corresponding pressure values and the totality is considered as a function of the pressure. These values are shown plotted on Plate 5. The next step is to get an equation and constants for the curve plotted from these values. The following equation was found to fit quite well;

$$f(p) = \frac{97.435}{p^2} + .01677p^{\frac{1}{2}} - .1858$$

VII. Equations for Specific Heat and Heat Content.

Having the characteristic equation in the form;

$$v = \frac{BT}{p} - \frac{m}{T^6} - f(p)$$

the equations for c_p and i are readily found by the method indicated in section III. Thus

$$\varphi(T) = \frac{m}{T^6}$$

$$\varphi'(T) = - \frac{6m}{T^7}$$

$$\varphi''(T) = \frac{42m}{T^8}$$

Then $c_p = F(T) + ApT \varphi''(T)$

$$= F(T) + \frac{42 \, Amp}{T^7}$$

The arbitrary function $F(T)$ must be determined from the experiments on values of c_p for ammonia. An excellent discussion of these experiments is contained in Goodenough and Mosher's work (Bulletin No. 66 p.74). After several trials the following linear form of the function was adopted;

$$F(T) = 0.43 + 0.0002T;$$

hence the equation for c_p is

$$c_p = 0.43 + 0.0002T + 42 \frac{Amp}{T^7}$$

The general expression for the heat content i (section III) is

$$i = F_1(T) + Ap\left[T\varphi'(T) - \varphi(T)\right] - Af_1(p) + i_\circ$$

But $F_1(T) = \int F(T)\, dT = 0.43T + 0.0001T^2$

$$A\left[T\varphi'(T) - \varphi(T)\right] = -\frac{7m}{T^6}$$

$$f_1(p) = \int f(p)\frac{dp}{\Lambda} = \frac{-97.435}{p} + 0.01118p^{3/2} - 0.1858p$$

The constant of integration $i_\circ$ gives a precise indication of the consistency of the inter-related equations from a thermo-dynamic standpoint. If the set of values of $i_\circ$ obtained by substituting the various temperatures with the corresponding saturation pressures in the i-equation and subtracting from the Bureau of Standards' experimental values of i is really a constant for the whole range of values, then the system of equations may be considered consistent, otherwise they are not. The calculated values of $i_\circ$ for the above i-equation are as follows;

t	-40	-27.967	-22	-4	14	32
T	419.6	431.633	437.6	455.6	473.6	491.6
p	10.279	14.697	17.370	27.813	42.60	62.87
$f_1(p)$	-2.0	-1.6	-1.5	-1.3	-1.3	-1.4
$F_1(T)$	198.1	203.7	207.4	216.6	225.9	235.7
$F_2(p,T)$	13.4	16.1	17.6	22.1	26.8	31.6
i B.of S.	519.1	523.8	526.0	532.4	538.1	543.3
$i_\circ$	332.4	334.5	334.7	336.6	337.7	337.8

t	50	68	86	104	122
T	509.6	527.6	545.6	563.6	581.6
p	89.91	125.15	170.2	226.73	296.6
f (p)	-1.5	-1.5	-1.4	-.8	.3
F (T)	244.9	254.3	264.3	273.6	283.8
F (p,T)	36.4	41.1	45.7	50.2	54.3
i B.of S.	547.7	551.2	554.0	555.6	555.0
i	337.7	336.5	334.0	331.1	325.8

Thus it is seen that the i○ value for -40° is 332.4 and that i○ increases as the temperature increases until at 32°, it has the maximum value, 337.8, then it decreases as the temperature increases until at 122° it has the value 325.8.   It thus appears that above equations are not as consistent as might be desired.

The final result seems to depend almost entirely on the initial choice of the form of the equation to fit the Perman and Davies' superheat points together with the Bureau of Standards' atmospheric saturation point.   The f(p) function depends solely on this choice as it is obtained by subtracting the values obtained from the chosen equation from the values of the specific volumes obtained by differentiating the pressure-temperature equation and substituting in the Clapeyron-Clausius volume relation.   The term obtained by integrating the perfect differential in the total heat differential equation also depends on the chosen form of the equation.   Thus it appears that the form of equation for the superheat volume curve at atmospheric

pressure has a very marked influence on the consistency of the
resulting system of equations.   As an illustration of this
influence on the f(p) curve see Plates 5, 6, and 7, where there
are shown three different curves resulting from three choices
of form and constants for the ψ(T) function.

Another form of equation tried for the specific volume
curve at constant pressure was as follows;

$$\frac{a}{T^5} + bT + c = \psi(T)$$

where a = $-1.46281 \cdot 10^{13}$

    b =   .043080

    c = -.05058

The curve passes through the 122°and 212° Perman and Davies
points and the Bureau of Standards' atmospheric saturation point
exactly and it passes near the other two Perman and Davies'
points as follows;

t	-4	32
T	455.6	491.6
(T)	18.8316	20.6302
P.& D.	19.154	20.78
Diff.	.322	.15
Diff.%	1.65	.57

It appears that within certain limits the choice of form

Plate 5. f(p) Curve for φ(T) with T^{-6} Term.

p	5.695	10.279	14.697	17.370	27.813	42.60
f(p)	2.5321	.8038	.3295	.2011	.0125	-.0227

p	62.87	89.91	125.15	170.2	226.73	296.6
f(p)	-.0074	.02184	.05080	.07240	.08870	.10406
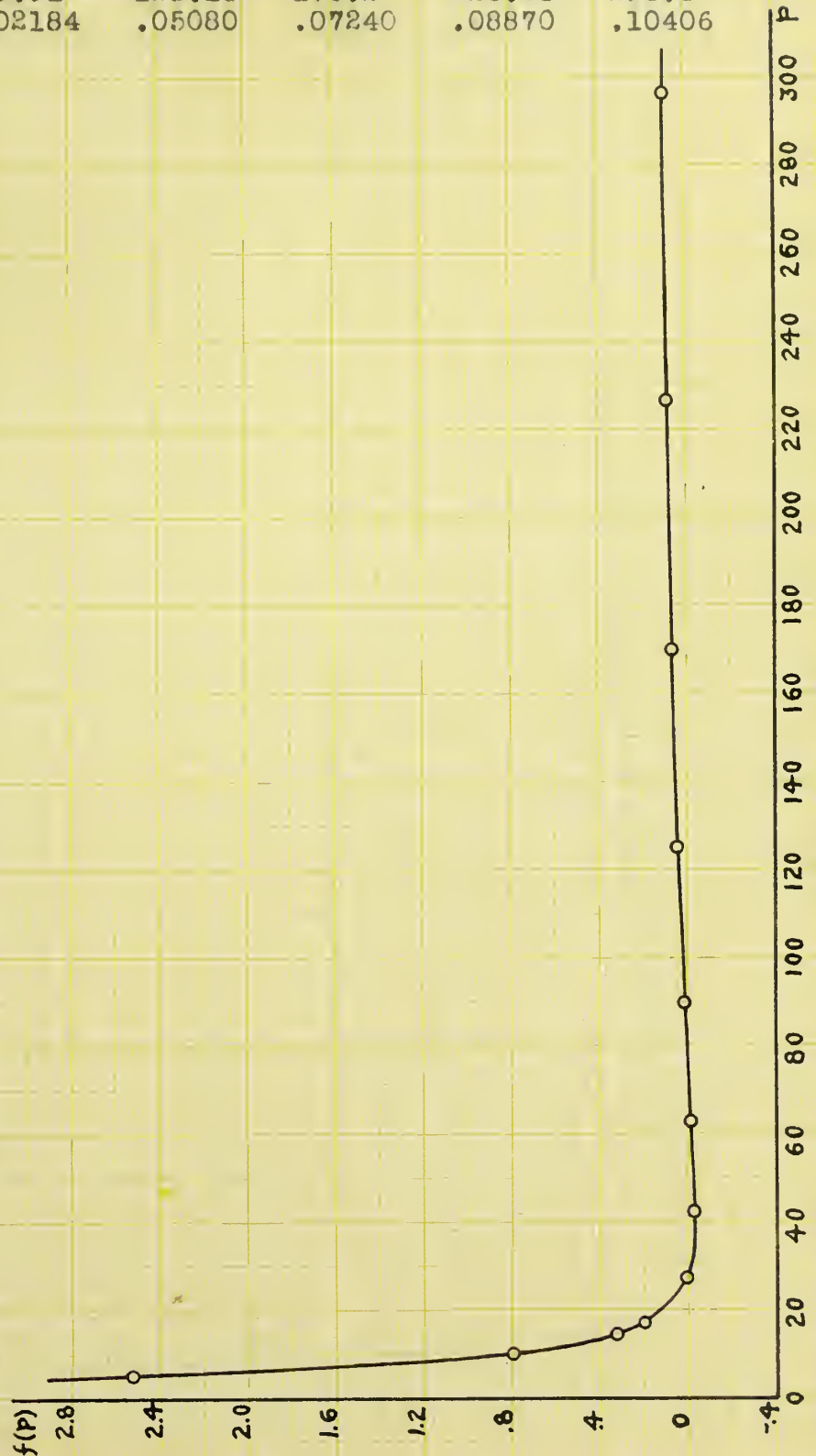
Plate 6. f(p) Curve for $\varphi(T)$ with T^{-5} Term.

p	5.695	10.279	14.697	17.370	27.513	42.60
f(p)	2.0793	.3752	.0506	-.0588	-.2036	-.2082

p	62.87	89.91	125.15	170.2	226.73	296.6
f(p)	-.1687	-.1201	-.0746	-.0389	.0104	.0156

Plate 7. f(p) Curve for φ(T) with T^{-4} Term.

p	5.695	10.279	14.697	17.370	27.813	42.60
f(p)	-1.353	.0460	.3896	.4685	.5451	.5028

p	62.87	89.91	125.15	170.2	226.73	296.6
f(p)	.4288	.3525	.2843	.2289	.1833	.1420

Plate 7. f(p) Curve for φ(T) with T^{-4} Term.
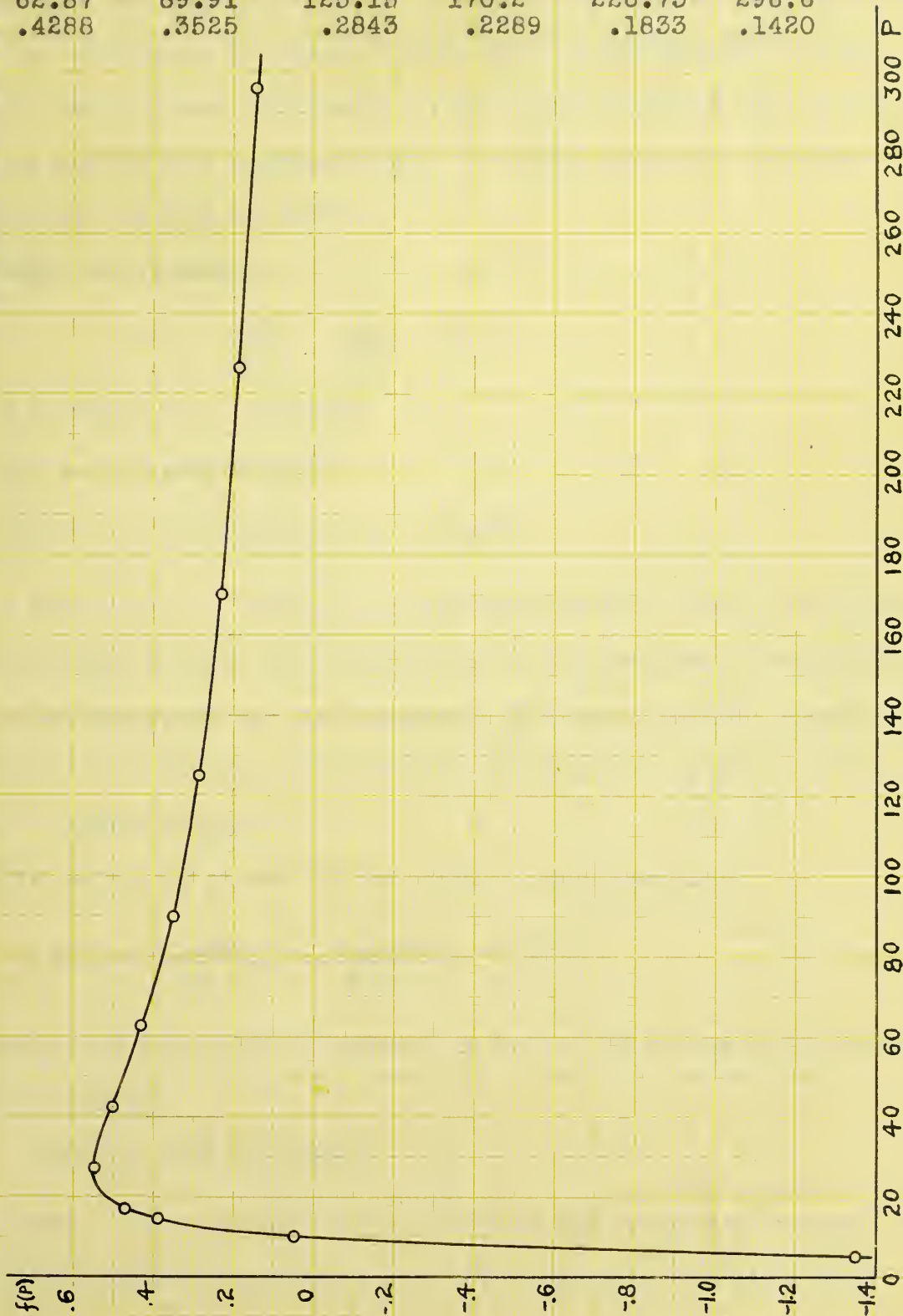
of equation and constants has not much influence on the approximation of the curve to these two points (1.65% against 1.62), while it has a great influence on the form required for the f(p) equation and on the constants for the F(T) equation and also on the form of the F(p,T) term.

From the equation

$$v = \frac{BT}{p} - \frac{m}{T^5} - f(p)$$

where B = b(14.697) = .633147

m = a = -1.46281·10^{13}

f(p) = c = -.05058 for p = 14.697

f(p) is obtained, as before, by subtraction from the calculated volumes obtained from the derivative of the pressure-temperature equation substituted in the Clapeyron-Clausius volume relation. The values obtained for f(p) when plotted gives quite a different curve, as shown by Plate 6.

This curve is given fairly well by the equation

$$f(p) = \frac{41.297}{p^{\frac{3}{2}}} - \frac{2.6708}{p^{\frac{1}{3}}} + .408$$

Following the same procedure as before the same expression for F(T), namely,

$$F(T) = .430 + .0002T$$

is obtained. The choice of the form of the specific volume curve at atmospheric pressure has less influence on this F(T)

function than on the others, although forms were tried which resulted in quite different constants for the F(T) equation.

The equation for the heat content takes the form,

$$i = .43T + .0001T - \frac{6mpA}{T^5} - A \int f(p)dp + i_0$$

The i_0 values obtained from this equation are as follows,

t	-40	-27.967	-22	-4	14	32
T	419.6	431.633	437.6	455.6	473.6	491.6
p	10.279	14.697	17.370	27.813	42.60	62.87
$f_1(p)$	-7.5	-7.3	-7.3	-7.6	-8.2	-8.9
$F_1(T)$	198.1	203.7	207.4	216.6	225.9	235.7
$F_2(p,T)$	12.8	16.1	17.6	23.0	29.0	35.6
i B.of S.	519.1	523.8	526.0	532.4	538.1	543.3
i_0	326.3	328.9	328.9	331.2	333.0	334.3

t	50	68	86	104	122
T	509.6	527.6	545.6	563.6	581.6
p	89.91	125.15	170.2	226.73	296.6
$f_1(p)$	-9.6	-10.4	-11.1	-11.5	-11.4
$F_1(T)$	244.9	254.3	264.3	273.6	283.8
$F_2(p,T)$	42.5	49.8	57.2	64.8	72.4
i B.of S.	547.7	551.2	554.0	555.6	555.0
i_0	335.7	336.3	335.8	335.0	332.2

It is seen that i_o for $-40°$ is 326.3 and that it increases with the temperature to $68°$ when it reaches a maximum of 336.3, then it decreases slowly as the temperature increases until at $122°$ it is 332.2; this set of values for i_o does not seem to be more nearly a constant than in the first case, although it seems to vary in the opposite direction somewhat.

Three other forms of equations for $\psi(T)$ and $f(p)$ were tried and the resulting sets of values for i_o were not as consistent as those shown.

An attempt was made to introduce a factor $(1 + ap)$ in the second term of the $\varphi(T)$ equation with the expectation that the set of values for i_o would be improved thereby, but the desired result was not obtained.

The alternative method suggested in section III was tried in order to see what specific heat values would be necessary to make i_o constant at the lower temperatures. Taking the second of the preceding formulations, let i_o be given the constant value 336.3 + c, where c denotes some constant. Keeping F_2 (p,T) and f_1 (p) the same, the new values of F_1 (T) are found to be;

t	-40	-22	-4	14
$F_1(T)$	188.1-c	200.-c	211.5-c	222.6-c
Diff.	11.9	11.5	11.1	11.1

t	32	50	68
$F_1(T)$	233.7-c	244.3-c	254.5-c
Diff.	10.6	10.0	

If these differences be divided by 18, the temperature difference, the quotients will be approximations to the derivative $\frac{di}{dT}$, that is to F(T), which is the arbitrary function in the specific heat equation.   These quotients range from 0.66 at -31° to 0.55 at 59°.   It appears, therefore, that for a constant series of values of io at the lower temperature range the specific heat must be very much higher than any of the experiments indicate.

A device which seemed to show promise of success was to consider the F (p,T) term in the i-equation in the following way. On inspection it is seen that this term is the product of TpA into the slope of the specific volume curve at atmospheric pressure plus this same product without the numerical factor due the power of T; hence by varying the slope of the curve at any particular temperature, it is possible to vary the value of io at this particular temperature in comparison with the rest of the range of values.   It is possible by repeatedly continuing this process of successive approximations to smooth out the whole set of values for io.   In this way the curvature and position of the curve is uniquely fixed to produce a consistent system of equations.   It seems reasonable to suppose that this uniquely fixed

curvature and position may actually be the same as that which will be determined by future experimentation. Lack of time prevented further investigation along these lines.

VIII. Conclusion.

As a result of this investigation, all the determining factors seem to indicate serious inconsistencies; (1) between the Bureau of Standards' atmospheric saturation volume point and the Perman and Davies' atmospheric superheat volume points; (2) between the spacing of the Specific heat curves at constant pressure and the conception of what this spacing should be, taking the properties of steam as a tentative guide; (3) between the specific heat curve at zero pressure required to make the set of values for i_0 a constant and experimental values of specific heats. It seems impossible to reconcile the first of these inconsistencies; and if eventually the Bureau of Standards' values of saturation volumes are validated, the Perman and Davies' must be regarded as inaccurate.

Reconciliation of the remaining inconsistencies is not so hopeless a task, although it seems likely that acceptance of the Bureau of Standards' results must require a revision of the previously accepted values of the specific heat.

It is hoped that in the near future, the Bureau of Standards will continue its splendid experimentation on the thermodynamic

properties of ammonia and that as a result of the data thus obtained, the entire question of the thermal properties of ammonia will be cleared up in a satisfactory way.